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(54) Title: NEUTRALIZED ACRYLIC COPOLYMER PRESSURE SENSITIVE ADHESIVES		
(57) Abstract		
<p>Neutralized acrylic copolymer PSA compositions having enhanced peel strength and shear properties have been formulated by incorporating less than 2 percent and greater than 0.5 percent by weight of (meth)acrylic acid into the polymer composition and neutralizing the free acid groups to a pH of 6.5 to 8. The PSA includes a tackifying resin.</p>		

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NEUTRALIZED ACRYLIC COPOLYMER PRESSURE SENSITIVE ADHESIVES

Field of the Invention

5 The present invention relates to tackified acrylic copolymer compositions and more particularly to pressure sensitive adhesive (PSA) compositions comprising a neutralized (meth)acrylic acid component.

10

Background of the Invention

According to the "Glossary of Terms used in the Pressure Sensitive Tape Industry," a pressure sensitive adhesive (PSA) is a material which is aggressively and
15 permanently tacky, adheres without the need of more than finger pressure, exerts a strong holding force, and has sufficient cohesiveness and elasticity that it can be removed from substrates without leaving a residue. A PSA for use as the adhesive backing on a label generally
20 requires good adhesion as reflected in tack measurements. On the other hand, PSAs used in tapes generally require good cohesion as reflected in shear measurements.

In PSA applications it is essential to have a good balance of adhesive and cohesive strength properties.
25 These properties of tack (adhesion) and shear (cohesion), however, are recognized as generally having an inverse relationship because cohesive strength generally depends on high molecular weight entanglements and/or cross-links between chains, whereas tack properties are generally
30 improved by low molecular weight species which result in enhanced ability for deformation and substrate wetting. A property balance is normally achieved by judicious choice of combinations of monomers. Small amounts of either acrylic or methacrylic acid are sometimes
35 incorporated to improve the cohesive strength for some applications such as PSA tapes where high shear power is required. However, in order to achieve the required shear strength, the acid concentration must usually be increased to a level which reduces adhesion properties.

Accordingly, there is a need for an emulsion polymerized acrylic composition which can simultaneously boost both shear and tack properties of PSA tapes and labels.

The emulsion polymerization of acrylic- containing
5 polymers is well known in the art. For example, U. S. Patent 4,540,739 to Midgley teaches an aqueous based pressure sensitive adhesive having improved shear properties. The PSA is prepared from a latex of one of the following monomer compositions: alkyl esters of
10 acrylic or methacrylic acid and a C₃-C₉ ethylenically unsaturated carboxylic acid; a C₄-C₈ conjugated diolefin, optionally a vinyl aromatic monomer, and a C₃-C₉ ethylenically unsaturated carboxylic acid; or a C₂-C₄ monoolefin, a vinyl ester, and an a C₃-C₉ ethylenically
15 unsaturated carboxylic acid. The resulting latex is neutralized to a pH of equal to or greater than about 6 with an alkali metal hydroxide or salt. The polymer may optionally have a molecular weight distribution so that from about 20 to about 55 weight percent has a molecular
20 weight greater than 320,000. The adhesive may also optionally include tackifiers and may be used in the manufacture of tapes and labels.

Japanese Kokai 83/22,492 discloses a PSA consisting of a vinyl monomer, an alkyl acrylate and an
25 ethylenically unsaturated carboxylic acid with one or two carboxyl groups. The PSA is prepared by adding univalent metallic ions to a copolymer emulsion obtained by emulsion polymerization of the monomer mixture.

Japanese Kokai 89/36,872 discloses a PSA consisting
30 of an acrylic emulsion that is neutralized and then treated with ethylene diamine tetracetic acid.

Japanese Application 83/226,973 discloses an acrylic emulsion containing a carboxylic acid monomer neutralized to pH 7 with ammonia or an amine. It is then treated
35 with an aziridine compound to provide a PSA.

Japanese Kokai 86/52,191 discloses a PSA emulsion polymer produced in two stages. The first stage involves the preparation of an acrylic emulsion from an acrylic ester plus (meth)acrylic acid, followed by neutralization
5 to pH 6-10 with an alkali metal salt. This emulsion provides the dispersant for the second stage polymerization in which butadiene and another monomer are added.

Japanese Kokai 86/50,516 discloses PSAs comprising
10 acrylic polymers treated with aqueous alkali. Bulk polymerization is followed by treatment with aqueous alkali which partially or completely neutralizes the carboxylic acid groups on the polymer and results in the formation of an emulsion.

15 Japanese Kokai 87/10,591 discloses a pressure sensitive adhesive tape produced by adding water and alkali to a bulk polymerized acrylic type copolymer having tackiness at room temperature and consisting mainly of monomers comprising methacrylic acid alkyl
20 esters and unsaturated monomers containing an acid group.

Japanese Application 82/48,643 discloses a pressure sensitive adhesive tape produced by polymerizing an acrylic copolymer comprising mainly (meth)acrylate esters and an unsaturated comonomer having acid groups, removing
25 unreacted monomers to obtain a solid product, adding aqueous alkali to the product to neutralize the acid groups, and coating one or both sides of the support tape with a water solution.

Japanese Application 83/58,530 discloses a process
30 for preparing a pressure sensitive adhesive tape from an acrylic copolymer having a weight average molecular weight of 10^4 - 10^6 and produced from methacrylic acid esters and unsaturated esters containing acid groups. The copolymers are neutralized and dispersed in a water
35 solution at an average granular diameter of 0.01 to 0.1 microns. A tape is coated with a water solution. The neutralizing step is said to be done in two stages.

U. K. Patent Application 2,111,484 discloses stabilizers for the emulsion polymerization for olefinic monomer and comonomer systems comprising the half esters of nonionic ethoxylates of the formula $R(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$ wherein R is a $\text{C}_8\text{-C}_{30}$ linear alkyl or $\text{C}_4\text{-C}_{18}$ mono-, di-, or tri-alkyl phenyl, R is linked to ethoxy by O, S, or N, and x is 4-10, with α,β -ethylenically unsaturated dicarboxylic acids, preferably maleic, citraconic and itaconic acids. Stable, low floc latices having good shear are said to be obtained and are useful as pressure and nonpressure sensitive adhesives. The olefinic unsaturated monomers are those of the vinyl and acrylic types.

U. S. Patent, 3,492,260 to Samour teaches an aqueous emulsion polymerization system for the preparation of an emulsion of latently crosslinkable polymers. One of the comonomers is an amic acid or an acid ester in salt form and one of the essential comonomers is selected from the group consisting of acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, cyanoethylacrylate and cyanoethylmethacrylate.

Summary of the Invention

A pressure sensitive adhesive (PSA) composition incorporating ionic molecular attractions is prepared from an emulsion of an acrylic copolymer and a tackifying resin. The acrylic copolymer comprises a lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, an upper alkyl (meth)acrylate, and acrylic or methacrylic acid at a concentration of greater than 0.5 and less than 2 weight percent. The copolymer is neutralized to pH of from about 6.5 to about 8. The copolymer by itself has a glass transition temperature (T_g) of from about -75°C to about -30°C , preferably from about -65°C to about -40°C . The tackifying resin preferably has a softening point of from about -20°C to about 150°C , more preferably from about 10°C to about 100°C . The tackified copolymer has a

T_g of from about -70°C to about 10°C , preferably from about -60°C to about -10°C .

The PSA, when coated onto a suitable substrate such as flexible polyester or polyolefin film, has both enhanced adhesive strength as measured by tack properties and cohesive strength as seen in shear properties, and is suitable for use in either or both label and tape applications.

In a preferred embodiment, the present invention comprises greater than 0.5 weight percent and less than 2 weight percent of a (meth)acrylic acid, from 0 to about 50 percent by weight, preferably from about 10 to about 35 percent by weight of a lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, from about 48 to about 99.5 percent by weight, preferably from about 63 to about 89.5 percent by weight of an upper alkyl (meth)acrylate ester and the acid groups are neutralized by a monovalent alkali metal base to pH of from about 6.5 to about 8. The resin tackifier is present in an amount of from about 40 to about 100 parts by weight per 100 parts by weight of the copolymer. The tackified copolymer product has a T_g from about -70°C to about 10°C , preferably from about -60°C to about -10°C . The PSA composition when adhered to stainless steel has a 180° peel of from about 7 to about 20 N/in., preferably from about 11 to about 20 N/in.; a loop tack of from about 10 to about 20 N/in., preferably from about 12 to about 20 N/in.; and a shear strength from about 44 to about 100 hrs. The PSA composition when adhered to polyethylene has a 180° peel of from about 5 to about 13 N/in., preferably from about 9 to about 13 N/in.; a loop tack from about 5 to about 13 N/in., preferably from about 9 to about 13 N/in.; and a shear strength from about 44 to about 100 hours.

In another embodiment of the present invention, a method for preparing a neutralized acrylic copolymer latex composition comprises the steps of: emulsifying

vinyl monomers comprising greater than 0.5 and less than 2 percent by weight (meth)acrylic acid, preferably from about 10 to about 35 percent by weight lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, and
5 preferably from about 63 to about 89.5 upper alkyl (meth)acrylate ester in an aqueous medium to form a monomer-in-water emulsion; polymerizing the emulsion to form an acrylic copolymer latex having a T_g from about -75°C to about -30°C; neutralizing the copolymer latex
10 with a base to pH of from about 6.5 to about 8; and providing in the latex a hydrocarbon tackifier in an amount of from about 40 to about 100 parts per weight per 100 parts by weight of the copolymer. The tackified copolymer has a T_g from about -70°C to about 10°C,
15 preferably from about -60°C to about -10°C.

In a further embodiment, the present invention comprises a pressure sensitive adhesive-coated article comprising a substrate having a coating of the neutralized resin-tackified acrylic copolymer on a
20 surface thereof. The PSA comprises a hydrocarbon resin having a molecular weight of from about 500 to about 5000 and a ring and ball softening point of -20°C to 150°C, preferably 10°C to 100°C, and an acrylic copolymer formed by emulsion polymerization. The copolymer comprises a
25 lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, an upper alkyl (meth)acrylate and (meth)acrylic acid present in an amount of greater than 0.5 percent by weight and less than 2 percent by weight of the copolymer. The emulsion is neutralized to pH from about
30 6.5 to about 8. The tackified copolymer product has a T_g from about -70°C to about 10°C, preferably from about -60°C to about -10°C. Substrates may be metallic, paper, plastic or cloth.

In yet a further embodiment, the present invention
35 is a laminate article comprising at least two opposing surfaces bonded by an adhesive composition. The adhesive comprises an acrylic copolymer formed by an emulsion

polymerization of a monomer mixture and a tackifying resin having a ring and ball softening point of from about 10°C to about 100°C. The copolymer comprises a lower alkyl (meth)acrylate ester or a non-acrylic vinyl
5 monomer, an upper alkyl (meth)acrylate and includes acrylic or methacrylic acid in an amount of greater than 0.5 percent by weight and less than 2 percent by weight. The acid groups are neutralized to a pH from about 6.5 to about 8. The tackified copolymer product has a T_g from
10 about -70°C to about 10°C, preferably from about -60°C to about -10°C.

Detailed Description of the Invention

15 The pressure sensitive adhesive (PSA) compositions of the present invention incorporate ionic attractions into emulsion polymerized acrylic copolymers to enhance the cohesive strength of the PSA, and at the same time enhancing adhesive strength or at least avoiding
20 significantly adversely affecting adhesive strength. The resulting PSA is thereby suitable for both label and tape applications. Adhesive strength may be actually improved with an improvement in cohesive strength for certain compositions in contradistinction to the prior art
25 wherein cohesive strength improvements are generally accompanied by adhesive strength reductions. It has been discovered that property improvements imparted by ionic attractions are limited to concentrations of acrylic and methacrylic acid less than about 2 and greater than 0.5
30 percent by weight of the copolymer. At 2 percent by weight and above, adhesion is adversely affected, whereas at 0.5 percent by weight and below, there is no cohesive strength improvement.

The neutralized acrylic copolymers which are an
35 ingredient of the present invention generally comprise a (meth)acrylic acid component, an upper alkyl (meth)acrylate ester component and a component selected from the group consisting of a lower alkyl (meth)acrylate

ester and a non-acrylate vinyl monomer. As used herein, the terms "acrylic" and "acrylate" denote a generalized material comprising in greatest extent an alkyl ester of acrylic or methacrylic acid. The term "(meth)acrylate" refers to either a methacrylate or an acrylate. The term "(meth)acrylic acid" refers to either methacrylic acid or acrylic acid.

In the present invention, free acid groups comprise acrylic or methacrylic acid, preferably acrylic acid, which are neutralized, preferably by a monovalent alkali metal base, to a pH of from about 6.5 to about 8.

Lower alkyl esters of (meth)acrylic acid preferably have 1 to 3 carbon atoms in the alkyl group. Examples of lower alkyl (meth)acrylate ester monomers include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and the like.

Upper alkyl esters of (meth)acrylic acid are defined as having 4 or more carbon atoms, usually up to about 14 carbon atoms, but preferably from 4 to about 8 carbon atoms in the alkyl group. Examples of upper alkyl (meth)acrylate ester monomers include n-butyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, isooctyl (meth)acrylate, and the like.

In addition to acrylic monomers, non-acrylic vinyl monomers may also be employed. Examples of some non-acrylic vinyl monomers include acrylonitrile, vinyl acetate, vinylidene chloride, styrene, methyl styrene, and the like.

The lower alkyl (meth)acrylate and non-acrylic vinyl monomer generally comprise from 0 to about 50 percent by weight, preferably from about 10 to about 35 percent by weight of the copolymer. The upper alkyl (meth)acrylate ester generally comprises from about 48 to about 99.5 percent by weight, preferably from about 63 to about 89.5 percent by weight of the copolymer. The (meth)acrylic acid component, as mentioned previously, comprises

greater than 0.5 percent by weight and less than 2 percent by weight of the acrylic copolymer.

The acrylic copolymers are neutralized to a pH in the range of 6.5 to 8. Suitable alkali metal bases for
5 neutralizing the copolymer include sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like. Other bases may also be used.

Tackifying resins suitable for the practice of the present invention may be a natural rosin or rosin ester
10 resin, a synthetic hydrocarbon resin, or the like. Hydrogenated resins may also be used. Tackifiers typically have a ring and ball softening point from about -20°C to about 150°C. Preferred tackifiers have a softening temperature from about 10°C to about 100°C.
15 PSAs suitable for labels or lamination adhesives typically include resins having a softening point from about 15°C to about 40°C. PSAs suitable for tapes typically utilize tackifying resins having a softening point from about 70°C to 100°C. Tackifying resins
20 suitable for use in the present invention generally have a molecular weight of from about 500 to about 5000, preferably from about 1500 to about 2500.

Hydrocarbon tackifiers are generally manufactured from C₉ aromatic monomers or C₅ aliphatic monomers or a
25 mixture thereof. These monomers are derived from the so-called C₉ and C₅ cuts in the fractionation of crude oil, or similar material. Aromatic hydrocarbon resins are available commercially under the trade designations ESCOREZ, CUMAR, ARCON, and the like; aliphatic
30 hydrocarbon resins are available under the trade designations ESCOREZ, PICCOTAC, ARCON, and the like. A particularly preferred tackifier is ESCOREZ-9271.

Naturally occurring resins suitable for use in the present invention may be rosin esters or terpenes such as
35 α -pinene, β -pinene, carene, limonene or other readily available terpinous materials, α -pinene and limonene being preferred. The material may be pure or the

commercially available concentrates such as gum
terpentine or α -pinene concentrates, which tend to be
mixtures of various terpinous materials. A suitable
natural resin contains from about 70 to 95 percent by
5 weight α -pinene, the remainder being other terpenes.
Examples of commercially available rosins and rosin
esters, which may be optionally hydrogenated, include
tackifiers sold under the trade designations FORAL,
HERCOLYN, HYDROTAC, STAYBELITE ESTER, PENTALYN, SYLVATAC,
10 ZONESTER and the like.

The tackifier resin is typically present in an
amount up to about 150 parts by weight per 100 parts by
weight of the copolymer, preferably from about 40 to
about 100 parts by weight per 100 parts by weight of
15 copolymer.

For the preparation of the PSAs of the present
invention, the polymerized composition should have a
suitable glass transition temperature (T_g). T_g of the
tackified copolymer product ranges from about -70°C to
20 about 10°C for PSA application, preferably from about
 -60°C to about -10°C . The polymerized and neutralized
products in the absence of the tackifying resin have a T_g
in a range from about -75°C to about -30°C , preferably
from about -65°C to about -40°C . If the glass transition
25 temperature is too high, ambient temperature tackiness
required for standard PSA applications is not generally
obtained. The copolymer glass transition temperature is
usually a function of the glass transition temperature of
the component monomer homopolymers, and therefore, may be
30 estimated based on a compositional weighted average of
the T_g of the component monomer homopolymers according to
the Flory-Fox equation. To achieve the low T_g , it is
generally necessary to avoid excessive amounts of high T_g
monomers such as lower (meth)acrylates, as well as the
35 high T_g materials such as styrene, acrylonitrile and the
like.

In a especially preferred embodiment, the neutralized acrylic PSAs when adhered to stainless steel have a 180° peel (PSTC #1) of from about 7 to about 20 N/in., preferably from about 11 to about 20 N/in.; a loop
5 tack (PSTC #5) of from about 10 to about 20 N/in., preferably from about 12 to 20 N/in.; and a shear strength (PSTC #7) of from about 44 to about 100 hrs or longer, preferably about 75 hrs or longer. When adhered to low energy surfaces such as polyethylene, PSAs of the
10 present invention have a 180° peel of from about 5 to about 13 N/in., preferably from about 9 to about 13 N/in.; a loop tack of from about 6 to about 13 N/in., preferably from about 9 to about 13 N/in.; and a shear strength of from about 44 to about 100 hrs or longer,
15 preferably about 75 hrs or longer.

Generally the reaction of acrylic monomers to form acrylic copolymers proceeds by emulsion polymerization and is well known to practitioners in the art. The emulsion medium includes water to adjust the solids
20 content of the emulsion and a surfactant to stabilize the formation of monomer-in-water emulsion and to act as a suspending agent for the solids in the final copolymer, which are dispersed in the aqueous medium both during and after the polymerization. The surfactants may be anionic
25 or nonionic, or a mixture thereof. Suitable anionic surfactants include alkali and alkaline metal salts of alkyl ether sulfate, alkyl sulfonates, alkyl phosphates, alkyl aryl sulfonates and the like. The polymerization may be catalyzed by a redox catalyst system or a free
30 radical generating agent such as a peroxide or episulfate. A molecular weight modifying agent such as t-dodecyl mercaptan or carbon tetrachloride may be employed. Up to this point, all polymerization procedures are conventional. Preferably immediately
35 following polymerization the latex is neutralized. The tackifier is typically incorporated last into the latex

emulsion, and if necessary pH adjusted to the desired target.

The composition is applied to the substrate using conventional coating techniques such as roller coaters, 5 blade coaters, meyer rods or stir coaters. The coated substrate is then dried usually by passing it through a heating tunnel or oven which may use circulating hot air or infrared lamps to dry the coated substrate. The drying time will be a function of a number of factors 10 such as the heat capacity of the substrate, the type of heating, the oven temperature, air velocities of circulating air is used and the rate of passage of the substrate through the oven or heating tunnel. The manufacturer may readily determine suitable 15 time/temperature relationships to determine optimum drying conditions in his equipment for the product.

The substrate should be coated with sufficient adhesive to provide a dry coat weight from about 10 to about 35 pounds per 3,000 square feet. Generally, in the 20 manufacture of tapes using a continuous sheet polymeric substrate dry coat weight of about 17-18 pounds per 3,000 square feet are used. In the manufacture of labels a dry coating weight from about 12 to about 18 pounds per 3,000 square feet is usually used. In the manufacture of 25 masking tape, a dry coating weight from about 25 to 35 pounds per 3,000 square feet is usually used.

The dried and cured latex coating produces an adhesive film suitable for PSA application, particularly in labels and tapes. Suitable substrates include 30 metallic, plastic, paper, cloth materials and the like. Examples of metallic substrates include aluminum, copper and steel and the examples of plastic substrates include polyesters, polyolefins, polyethylene terephthalate, and the like. The manufacturing process for preparing 35 adhesive tapes and labels is well known in the art.

In certain embodiments of the practice of this invention, the adhesives formed find application as non-pressure sensitive adhesives such as, for example, laminating adhesives, binders for woven and nonwoven
5 fabrics and binders for pressed wood production. For example, embodiments useful as laminating adhesives have high peel strength but low shear properties. Such adhesives can be used to join two or more sheets of material together such as joining a layer of wood or a
10 multiple layer of wood to form a plywood product.

PSA test samples were prepared from a knife-coated layer of the copolymer latex (about 60-65 percent total solids) on MYLAR film. The film was dried in an air circulating oven for 3 min at 110°C and had an adhesive
15 coating of about 1.5 mils. The test adhesive was bonded to a stainless steel, glass or polyethylene substrate for the performance test in question.

The 180° peel adhesion test followed PSTC-1. Briefly, the test consists of measuring the force
20 necessary to strip or delaminate an adhesive tape as prepared above. A 1" wide tape is adhered to a clean substrate bar and the bar is mounted in an Instron tester. The free end is pulled away at a 180° angle at a rate of 12 inches per minute. Values are reported in
25 newtons (N) per inch.

The loop tack test followed a modified PSTC-5 procedure, and is measured by forming a loop from a 1" x 8" strip of tape, adhesive face out, inserted into the clamp of an Instron tester and moving the loop at a rate
30 of 12 inches/min onto a substrate panel then removing the strip at the rate of 12 inches/min after 2 in.² of contact is made. The highest force required to remove the loop is reported.

The shear strength is measured by PSTC-7. Briefly,
35 a 1" x 1" overlap of a sample tape is adhered to a substrate material and a 1 kg weight suspended

vertically. The test measures the cohesive strength of the sample over time.

The foregoing invention having now been described, the following examples are to further teach the preferred
5 embodiment and best modes for practicing the described invention and to aid others in the practice of the scope of such invention herein provided.

10 Examples 1-2 and Comparative Examples 1-12

Acrylic copolymers suitable for use in the present invention were polymerized in an emulsion polymerization process. Monomers were selected from 2-ethylhexyl acrylate (2EHA), ethyl acrylate (EA), vinyl acetate (VA)
15 and/or methyl methacrylate (MMA). Acrylic acid (AA) in varying concentrations provided the free acid groups. The tackifying resin was ESCOREZ-9271. PSA compositions were formulated and a series of tests were performed on both neutralized and non-neutralized samples to compare
20 adhesive and cohesive strength for different acid and tackifier concentrations. Adhesive strength was measured for stainless steel (SS), glass and polyethylene (PE) substrates by the 180° peel and/or the loop tack tests while cohesive strength was measured for a stainless
25 steel substrate by the shear adhesion test. Data are presented in Table I.

TABLE I

5

EXAMPLE	COMPOSITION (wt %)						pH ±0.5	180° PEEL (N/in.)		LOOP TACK (N/in.)			SHEAR (hr) SS 1" x 1" x 1kg	
	ZEHA	EA	VA	MMA	AA	RESIN		SS	GLASS	SS	GLASS	PE		
10	Comp. 1	75	21	--	--	4	0	4.1	3.1		1.9			0.013 ^b
	Comp. 2	75	21	--	--	4	0	7.1	13.7		7.7			0.135 ^b
	Comp. 3	79.5	--	12.5	7.5	0.5	0	4.5	9.1	8.1	9.4	10.1	5.5	7.7 ^c
15	Comp. 4	79.5	--	12.5	7.5	0.5	0	7	9.8	9.1	8.9	11.3	5.9	8.2 ^c
	Comp. 5	79.5	--	12.5	7.5	0.5	30	4.5	12.4	13.0	8.0	11.1	6.9	21.5
	Comp. 6	79.5	--	12.5	7.5	0.5	30	7	10.5	10.0	10.6	9.8	8.3	--
20	Comp. 7	79.5	--	12.5	7.5	0.5	40	4.5	13.2	12.3	5.0	10.1	5.8	13.4
	Comp. 8	79.5	--	12.5	7.5	0.5	40	7	11.0	12.5	11.3	14.0 ^a	8.6	67.3
	Comp. 9	79.1	--	12.4	7.5	1.0	0	4.3	6.8	6.0	7.4	8.6	6.3	2.2 ^c
25	Comp. 10	79.1	--	12.4	7.5	1.0	0	7	7.3	5.5	8.9	10.0	8.6	7.2 ^c
	Comp. 11	79.1	--	12.4	7.5	1.0	30	4.3	11.5	12.3	12.8	13.3	10.3	15.5
	1	79.1	--	12.4	7.5	1.0	30	7	10.1	9.8	12.2	11.6	10.6	23.6
30	Comp. 12	79.1	--	12.4	7.5	1.0	40	4.3	15.8 ^a	16.3 ^a	12.5	13.2	9.7	6.5
	2	79.1	--	12.4	7.5	1.0	40	7	15.3 ^a	15.0	12.3	14.4	12.2	195.0 ^a

^a - adhesive transfer/cohesive failure

^b - 1" x 1" x 2kg

40 ^c - 1/2" x 1" x 1kg

Data appearing in Table I indicate that the neutralized samples have a significantly enhanced shear property compared to the non-neutralized samples. At the same time, the tack properties of the neutralized samples were concurrently either equivalent to the tack of the non-neutralized samples or enhanced as well. Note Comparative Examples 7 and 8 where the shear improved by 5 times and the loop tack increased about 50 percent for polyethylene, 40 percent for glass and over 100 percent for stainless steel in the neutralized sample. In

Example 2 and Comparative Example 12, neutralization improved the shear by 30 times and tack properties remain essentially the same or slightly improved. The tackifier in the PSA formulation had a beneficial effect on the entire range of properties.

Examples 3-8 and Comparative Examples 13-23

Acrylic copolymers were prepared similarly to Examples 1-2 and Comparative Examples 1-12, i.e. with the same relative proportions of 2EHA, VA and MMA, except that copolymer compositions were varied particularly regarding acid concentration including methacrylic acid (MAA). PSA compositions were then formulated and testing was conducted. The results are presented in Table II.

TABLE II

5					pH	180° PEEL		LOOP TACK		SHEAR (hr)
	EXAMPLE	COMPOSITION (wt %)			±0.5	(N/in.)		(N/in.)		SS 1"x1"x1kg
		AA	MAA	RESIN		SS	PE	SS	PE	
10	Comp. 13			30	---	14	9	13	10	71
	Comp. 14	0.5		30	7	14	7.7	13	9.5	75
	Comp. 15	0.5		40	7	19 ^a	12 ^a	15	10	48
15	Comp. 16		0.5	30	7	15	6.8	9.5	8.2	12
	3		1	30	7	14	8.1	12	8.2	45
20	Comp. 17		2	30	7	11	6.3	11	7.7	100+
	Comp. 18		2	50	7	18	5.0	12	9.5	100+
	Comp. 19		3	30	7	8.6	5.0	8.2	4.5	100+
25	Comp. 20		4	40	7	7.7	4.1	6.4	3.6	100+
	4	1		30	7	10	7	12	10	100+
30	5	1		40	7	14	9	15	12	100+
	6	1		50	7	15	9 ^a	15	3 ^a	100+
	7	1.5		30	7	8	9	9	7	100+
35	8	1.5		40	7	8	10	10	8	100+
	Comp. 21	2		30	7	10	7	13	9	100+
40	Comp. 22	2		40	7	11	9	13	10	100+
	Comp. 23	2		50	7	19	5 ^a	17	4 ^a	100+
	Target					13	9	13	12	75
45										

a - adhesive transfer/cohesive failure

Results appearing in Table II indicate that while shear improved with increasing acid concentration, there was a general upper limit of desired acid groups above which the tack properties tended to fall off. Also, acrylic acid containing samples had superior properties overall to those samples containing methacrylic acid.

The foregoing description of the invention is illustrative and explanatory thereof. Various changes in the materials, apparatus, and particular parts employed will occur to those skilled in the art. It is intended
5 that all such variations within the scope and spirit of the appended claims be embraced thereby.

Claims:

1. A pressure sensitive adhesive composition, comprising a latex of:
 - an acrylic copolymer formed by polymerizing a monomer mixture emulsified in an aqueous medium, said monomer mixture comprising a lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, an upper alkyl (meth)acrylate ester and greater than 0.5 percent by weight and less than 2 percent by weight of a (meth)acrylic acid, said copolymer having a glass transition temperature of from about -75°C to about -30°C;
 - a tackifying resin; and
 - a base in an amount effective to obtain a pH in said latex of from about 6.5 to about 8.
2. The pressure sensitive adhesive composition of claim 1, wherein said copolymer glass transition temperature is from about -65°C to about -40°C.
3. The pressure sensitive adhesive composition of claim 1, wherein said tackified copolymer has a glass transition temperature of from about -70°C to about 10°C.
4. The pressure sensitive adhesive composition of claim 1, wherein said tackified copolymer has a glass transition temperature of from about -60°C to about -10°C.
5. The pressure sensitive adhesive composition of claim 1, wherein said tackifier is selected from the group consisting of rosins and hydrocarbon resins.
6. The pressure sensitive adhesive composition of claim 1, wherein said tackifying resin comprises a petroleum hydrocarbon resin having a softening point of from about -20°C to about 150°C and a molecular weight of from about 500 to about 5000.

7. The pressure sensitive adhesive composition of claim 6, wherein said softening point is from about 10°C to about 100°C.
8. The pressure sensitive adhesive composition of claim 6, wherein said softening point is from about 15°C to about 40°C.
9. The pressure sensitive adhesive composition of claim 6, wherein said softening point is from about 70°C to about 100°C.
10. The pressure sensitive adhesive composition of claim 1, wherein said monomer mixture comprises from 0 to about 50 percent by weight of said lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer and from about 48 to 99.5 percent by weight of said upper alkyl (meth)acrylate ester.
11. The pressure sensitive adhesive composition of claim 1, wherein said monomer mixture comprises from about 10 to about 35 percent by weight of said lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer and from about 63 to about 89.5 percent by weight of said upper alkyl (meth)acrylate ester.
12. The pressure sensitive adhesive composition of claim 1, wherein said neutralizing agent comprises an alkali metal base.
13. The pressure sensitive adhesive composition of claim 1, wherein said composition when adhered to stainless steel substrates has a 180° peel of from about 11 to about 20 N/in., a loop tack of from about 12 to about 20 N/in. and a shear strength of from about 44 to about 100 hrs and said composition when adhered to polyethylene substrates has a 180° peel of from about 9 to about 13 N/in., a loop tack of from about 9 to about 13 N/in. and a shear strength of from about 44 to about 100 hrs.
14. A method for preparing a pressure sensitive adhesive latex composition which comprises the steps of:

emulsifying vinyl monomers comprising greater than 0.5 percent by weight and less than 2 percent by weight (meth)acrylic acid, a lower alkyl (meth)acrylate ester or a non-acrylic vinyl monomer, and an upper alkyl (meth)acrylate ester;

polymerizing said emulsified monomers to form an acrylic copolymer latex, said copolymer having a glass transition temperature of from about -75°C to about -30°C;

neutralizing said latex to a pH of from about 6.5 to about 8; and

providing a tackifying resin in said latex.

15. The method of claim 14, wherein said tackified copolymer has a glass transition temperature of from about -60°C to about -10°C.
16. The method of claim 14, wherein said tackifier is selected from the group consisting of rosins and hydrocarbon resins.
17. A substrate coated with the latex of claim 1.
18. The coated substrate of claim 17, wherein said latex is dried to form a pressure sensitive adhesive.
19. The coated substrate of claim 17, wherein the substrate is selected from the group consisting of metals, plastic, paper and cloth.
20. A laminate article, comprising at least two materials having opposing surfaces bonded by the pressure sensitive adhesive composition of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/04798

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 09 J 133/08, C 09 J 7/02, B 32 B 7/12						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 09 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 09 J
Classification System	Classification Symbols					
IPC5	C 09 J					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹						
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
P,X	US, A, 4983656 (ITO ET AL) 8 January 1991, see column 3, line 6 - line 15; column 3, line 64 - column 4, line 2; column 4, line 61 - line 65; column 6, line 64 - line 66 column 7, pages 66-67 <div style="text-align: center; margin-top: 20px;">--</div>	1-20				
X	DE, B2, 2020496 (ROHM AND HAAS CO.) 11 June 1981, see column 2, line 31 - line 40; column 2, line 55 - column 3, line 17; column 9, line 16 - line 24; column 9, line 32 - line 33 exemple 3 <div style="text-align: center; margin-top: 20px;">--</div>	1-20				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search <div style="border: 1px solid black; padding: 2px; text-align: center;">18th October 1991</div>	Date of Mailing of this International Search Report <div style="border: 1px solid black; padding: 2px; text-align: center;">20. 11. 91</div>					
International Searching Authority <div style="border: 1px solid black; padding: 2px; text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorizing Officer <div style="border: 1px solid black; padding: 2px;"> </div>					

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	WO, A1, 9006976 (AVERY INTERNATIONAL CORPORATION) 28 June 1990, see page 2, line 30 - page 3, line 4; page 5, line 1 - line 20; page 8, line 1 - line 8; page 13, line 8 - line 10 -- -----	1-20

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/04798**

SA 49756

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/08/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4983656	08/01/91	JP-A- 1234485	19/09/89
DE-B2- 2020496	11/06/81	BE-A- 749689	28/10/70
		CA-A- 945296	09/04/74
		CH-A- 535825	15/04/73
		FR-A- 2040310	22/01/71
		GB-A- 1317931	23/05/73
		NL-A- 7006227	30/10/70
		SE-B-C- 362892	27/12/73
		US-A- 3740366	19/06/73
WO-A1- 9006976	28/06/90	EP-A- 0401226	12/12/90

For more details about this annex : see Official Journal of the European patent Office, No. 12/82